

Functionalization of Carbon Nanotubes Using Atomic Hydrogen from a Glow Discharge

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ABSTRACT

We have functionalized single walled carbon nanotubes (SWNTs) with atomic hydrogen generated in a cold plasma. A band at 2924 cm^{-1} ($3.4\text{ }\mu\text{m}$), characteristic of the C–H stretching mode, is observed using Fourier transform infrared spectroscopy. Additional confirmation of functionalization is provided by irradiating with atomic deuterium. A band in the region 1940 cm^{-1} ($5.2\text{ }\mu\text{m}$) to 2450 cm^{-1} ($4.1\text{ }\mu\text{m}$) corresponding to the C–D stretching mode is confirmed and another weak band in the region 1050 cm^{-1} ($9.5\text{ }\mu\text{m}$) to 1300 cm^{-1} ($7.7\text{ }\mu\text{m}$) corresponding to C–D bending mode is also seen. Our approach using a glow discharge provides a clean gas-phase process to functionalize SWNTs for further application development.

Single-walled carbon nanotubes (SWNTs) are being considered for nanoelectronic devices, hydrogen storage, and numerous other applications. Chemical processing methods that allow for the direct manipulation and tuning of the chemical and physical properties are needed for further application development. Gas phase functionalization techniques could prove extremely useful to fabricate sensors and devices based on SWNTs.^{1,2} One of the current challenges in fabricating large arrays of SWNT devices is the lack of selectivity in obtaining nanotubes with the desired electronic properties. Therefore, there is a need for developing techniques for the post-growth manipulation of the electrical properties of the nanotubes. Fluorination of the nanotubes, for example, has been shown to alter the electrical properties of nanotubes.³ There have been other limited reports^{4–6} on functionalization of SWNTs with various species by high-temperature gas exposure or wet chemistry, resulting in a change of physical or chemical properties.

Here we report a clean, low-temperature process for the functionalization of nanotubes. This approach using a glow discharge, to generate the necessary precursors, is suitable for attaching a wide variety of chemical groups to the nanotubes. Here we demonstrate functionalization of SWNTs with atomic hydrogen and present supporting evidence from in situ Fourier transform infrared spectroscopy (FTIR). Introduction of C–H bonds in SWNTs is expected to alter transport properties that may lead to useful semiconducting devices. Also, hydrogenated nanotubes may impart radiation

shielding properties to composites for space applications. FTIR has been previously used for analysis of nanotube samples.^{7–9} Kuhlmann et al. reported⁷ weak absorptions at 1598 ± 3 and $874 \pm 2\text{ cm}^{-1}$ in SWNT and 1590 and 868 cm^{-1} in polycrystalline graphite samples. The intensity of the band at 868 cm^{-1} is ~ 0.015 absorbance unit or 96.6% transmission. Since many of these bands are weak, care must be taken to ensure that the collection of the spectrum is not masked by background interferences.⁸ Kastner et al.⁹ were able to observe the weak band at 1575 cm^{-1} by using a vacuum spectrometer where the background absorption due to water vapor is eliminated.

In a cold plasma enhanced gas phase approach, the energy is supplied to the flowing gas at a fraction of a Torr pressure by a radio frequency (RF) generator and efficient power transfer is achieved through tuning a matching network. This produces a glow discharge with characteristic high electron energies. The temperature of the gas is typically 350–1000 K, which is much lower than that of the electrons at a few electronvolts. The gas temperature in our experiments is expected to be on the lower side of this range due to the low discharge pressure. The discharge produces electrons by ionization and radicals by dissociation, thus providing the atomic hydrogen for functionalization. The discharge may also introduce defects in CNTs that will serve to reduce the activation energy for chemisorption.

It is important to note that while the H_2 plasma is on, CNTs are exposed to harmful vacuum UV radiation (Lyman- α) produced in the plasma that can dissociate some of the C–H bonds as they are formed. It is known that UV irradiation

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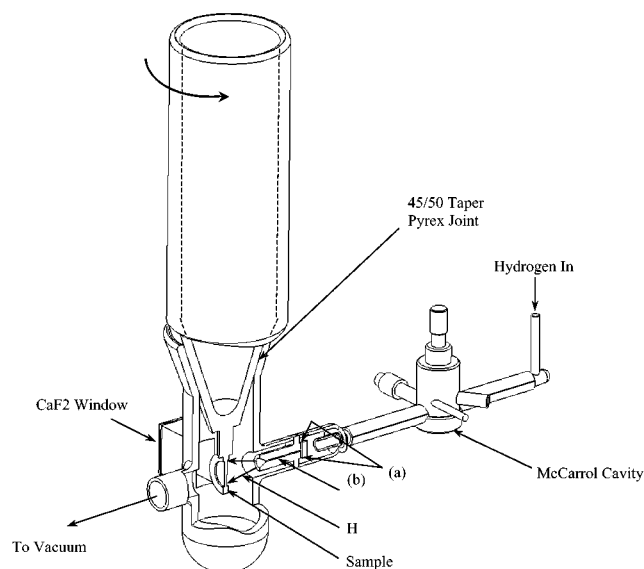


Figure 1. Apparatus to irradiate SWNTs by H atoms produced in a microwave discharge. H atoms enter through two 1 mm holes (a) in a Teflon plug at 90° to the target. This hole is joined by another 1 mm hole (b) through the center of the plug directing the H atoms in a beam to the target.

decreases the intensity of the C–H stretching feature in hydrogenated carbon materials,^{10–12} and therefore it is important to ensure that the rate of C–H bond formation is higher than the rate of destruction of the C–H bond by UV radiation. Mennella et al. have removed the UV radiation and shown that C–H modes are activated in nanosized hydrogen-free carbon particles by exposure to atomic hydrogen.¹³ Since we have no control over the penetration depth of the H atoms or the amount of UV radiation in a conventional discharge chamber, we designed a new apparatus to eliminate exposure of the CNT sample to UV radiation while permitting H atoms to constantly impinge on the sample.

A microwave discharge is used to generate atomic hydrogen (Figure 1). The application of microwave discharge sources for the production of intense beams of atomic, radical, and metastable species is well established. The source consists of a Pyrex tube (inner diameter of 10 mm and 1 mm thickness) inserted in a McCarroll cavity operated at 2.45 GHz. Microwave power is supplied by an Ophos microwave generator (model MPG 4M). The input and reflected powers were 70 and 48 W, respectively. The exit end of the tube is connected to a vacuum chamber (in which the sample is located) through a Teflon plug with a 1 mm bore down the center that collimates the H atom streaming toward the target. This aperture allows the buildup of gas needed for a localized discharge.¹⁴ To prevent UV radiation from hitting the sample, the entrance hole of the Teflon plug is designed off-axis, which allows only H atoms to pass.

We used a special glass cryostat where a calcium fluoride window coated with purified SWNTs is fastened in the center of the cryostat. The cryostat is on the end of a Dewar container that can be filled with liquid nitrogen. However, all of our functionalization studies were carried out at room temperature. The sample can be rotated to any position as

the bottom shroud with two CaF₂ windows is fixed and the top cryostat and the shroud are connected by a ground glass joint. This allows in situ recording of the spectra during the irradiation process and monitoring the progress of functionalization in real time. A Thermo Nicolet Nexus 670 FTIR at 4 cm^{−1} resolution was used in this study. A vacuum FTIR spectrometer (Bomem Model DA 8 at 4 cm^{−1} resolution) was also used, when necessary, to avoid interference from water and CO₂.⁹ Before starting the irradiation, a spectrum of the SWNTs is always taken to obtain the background signal.

The pressure of H₂ gas at the entrance of the chamber was maintained at 500 μmHg, while the pressure at the exit of the shroud is about 1 μmHg. The pressure difference creates a beam of H atoms hitting the SWNTs on CaF₂ substrate. HiPCO derived SWNT samples provided by Rice University¹⁵ were used in this study. Purification of the SWNTs was carried out by transferring 50 mg of the sample to a 50 mL flask with the addition of 25 mL of concentrated HCl and 10 mL of concentrated HNO₃. The solution was heated for 3 h and constantly stirred with a magnetic stirrer in a reflux apparatus equipped with a water-cooled condenser. This was done to remove unwanted iron and graphite nanocrystallites. The resulting suspension was then transferred into centrifuge tubes and spun-down at 3220g for 30 min. After pouring off the supernatant, the solid was resuspended and spun-down (30 min) three times in deionized water. Next, the solid was treated with NaOH (0.01 M) and centrifuged for 30 min. We qualitatively confirmed the purity of the SWNTs before and after purification using transmission electron microscopy (data not shown here). As evidenced by TEM, removal of the Fe nanoparticles was accomplished, and the crystallinity of the SWNTs was maintained. They appeared to be nanotube bundles with tube ends capped by half fullerenes. Finally, the sample was dried using a vacuum oven kept at 60 °C overnight. The SWNTs were then suspended in CCl₄ in order to deposit a film of SWNTs on the CaF₂ windows.

It is important to ascertain if SWNT and CaF₂ have any hydrocarbon impurity. For this reason, a film of SWNT on CaF₂ substrate was heated to 780 °C for 15 min. An ultrahigh purity 99.999% Ar gas flow was maintained during the entire heating and cooling process of the SWNT on CaF₂ substrate. Total hydrocarbon impurity in the argon gas was <1 ppm, and the balance were the sum of N₂, O₂, H₂, CO₂, and H₂O. Inspection of the C–H stretching vibration region of the spectrum clearly showed that both SWNT and CaF₂ substrate are free of hydrocarbon impurities to start with, as we did not find any trace of C–H bands in this region of the spectrum. To observe the C–H vibrations exclusively due to functionalization of SWNTs by irradiating with H atom from the microwave discharge, it is important to determine the position and intensity of C–H vibrations due to absorption (by the nanotubes) of hydrocarbon impurities present in the hydrogen gas used in the discharge. The H₂ gas is 99.9999% pure with moisture and hydrocarbon as trace impurities. H₂ in our experiments was passed through liquid nitrogen trap to eliminate water and possible higher hydro-

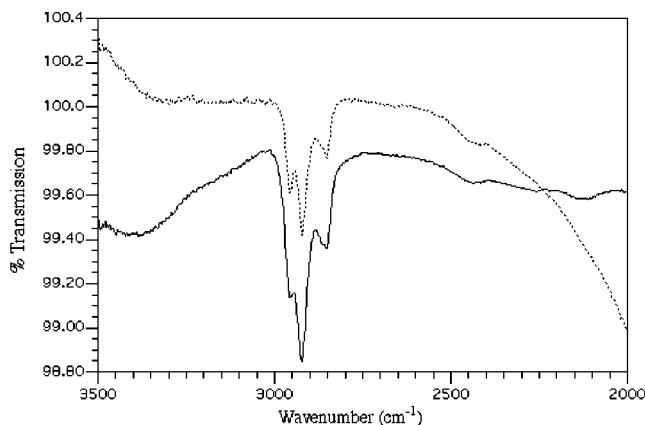


Figure 2. Spectra due to 6.5 h of H_2 flow over SWNT on CaF_2 (top). Also shown in the spectra after 6.5 h of H atom irradiation on the sample (bottom). More than double the intensity and shift in peak position is noticed on H atom irradiation.

carbon impurities. The hydrocarbon impurity is expected to be primarily methane because of employing the 77 K trap. We collected FTIR spectra (see Figure 2) of SWNTs exposed to just the H_2 gas flow (with no discharge, for 6.5 h). The band at about 2924 cm^{-1} is due to the C–H stretching mode on absorption of the CH_4 impurity by the SWNTs. The appearance of this band is not surprising since carbon nanotubes are known to be very good absorbers for hydrocarbons.¹⁶ Figure 2 also shows the spectra when the SWNTs are irradiated by H atoms from the discharge. Note that the gas flow rate, exposure time, and position of the SWNTs on the substrate are all identical to draw meaningful comparison of the spectra with and without the discharge. The increase in intensity of the C–H band in Figure 2 can be unambiguously attributed to functionalization by the H atoms from the discharge. We have measured the band intensity in both cases by measuring the area under the band after the bands are converted to absorbance scale. The area under the band for the case with the discharge-on is found to be a little over twice the area under the band for the case where a H_2 flow was maintained with no discharge. This increase in band intensity is due to functionalization of SWNT with atomic hydrogen.

The important result is that H atom irradiation on SWNTs produced a band at 2924 cm^{-1} ($3.4\text{ }\mu\text{m}$) with subfeatures at 2955, 2924, 2871, 2863, and 2854 cm^{-1} typical of the C–H stretching vibrations in CH_2 and CH_3 groups. There is no evidence for aromatic C–H modes ($\sim 3040\text{ cm}^{-1}$). We are not able to see the corresponding bending mode because it is obscured by a strong water band from the background of the Thermo Nicolet Nexus 670 FTIR spectrometer. Figure 3 shows the spectra in the range $1300\text{--}1800\text{ cm}^{-1}$ from the vacuum FTIR spectrometer for the sample exposed to H_2 gas flow only (with no discharge) and the sample exposed to atomic hydrogen irradiation. Based on the functionalization of carbon grains by the H atom in ref 13, we should expect the C–H bending mode in SWNT at around 1378 and 1457 cm^{-1} . We indeed find two bands at 1370 and 1459 cm^{-1} that may be the bending mode of C–H vibrations in SWNT on functionalization by H atom. There are two additional

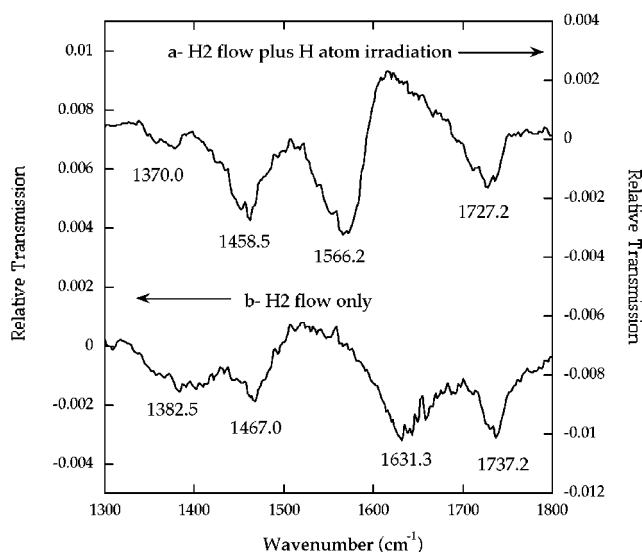


Figure 3. FTIR spectra of sample exposed to H atom irradiation from the discharge. The bands at 1370 and 1459 cm^{-1} are due to C–H bending mode in SWNT on functionalization with H atom. The band at 1566 cm^{-1} may correspond to broad and asymmetric band at 1575 cm^{-1} in unfunctionalized SWNT. The band at 1727 cm^{-1} may correspond to the C=C double bond or the C=O bond in the carbonyl group. FTIR spectra of SWNT exposed to only H_2 gas flow with no discharge is also shown. The bands at 1382 and 1467 cm^{-1} are from SWNT on CH_4 absorption. The shift in band position due to H atom functionalization (top) is noticeable. A similar shift is noticed for 1631 and 1737 cm^{-1} .

peaks at 1566 and 1727 cm^{-1} in this spectra. The band at 1566 cm^{-1} may correspond to the broad and asymmetric band at 1575 cm^{-1} in unfunctionalized SWNT⁹ and the band at 1727 cm^{-1} may correspond to C=C double bond or C=O bond in carbonyl group.⁶ The oxygen atoms may originate as an impurity with the hydrogen and carbon nanotubes known to be susceptible to oxygen adsorption even at very low pressures.^{2,13} It is noted that the intensity of the peaks in Figure 2 does not change regardless of the irradiation time from 1 to 7 h. Future controlled experiments will determine the minimum irradiation time required for functionalization and the extent of hydrogen coverage, as these are all issues of importance in applications.

To further confirm the functionalization results, we functionalized SWNT with D atoms by replacing hydrogen gas with deuterium gas in the microwave discharge. Figure 4 shows the presence of two weak bands in the region $2000\text{--}2250\text{ cm}^{-1}$ corresponding to the C–D stretching mode in functionalized SWNT by the D atom. Also shown are the spectrum of the same SWNT on the CaF_2 substrate with only the D_2 gas flow and the background spectra of the same SWNT sample prior to gas flow or striking the discharge. The D_2 gas (Matheson Gas Products) is 99.5% pure and the remainder is the sum of N_2 , O_2 , D_2O , and hydrocarbon as impurities. As expected, the hydrocarbon impurity in deuterium produced bands at 2924 cm^{-1} due to absorption of CH_4 during 10 h of deuterium flow over SWNT. Since there is no trace of the C–D band during 10 h of deuterium flow, it is concluded that the D_2 cylinder does not contain any deuterated hydrocarbons impurity. Therefore, the C–D

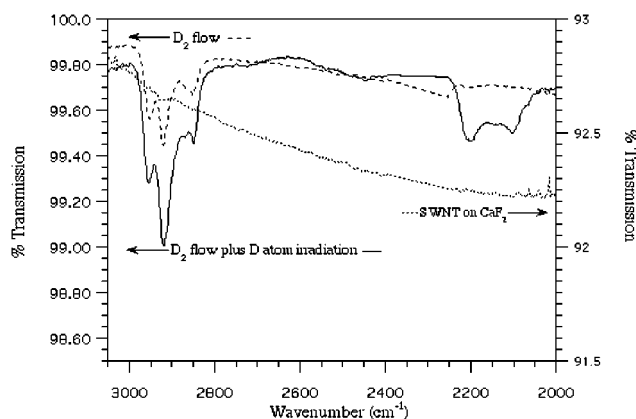


Figure 4. FTIR spectra of SWNTs exposed to atomic D irradiation from a D₂ discharge. Weak peaks at 2100 and 2201 cm⁻¹ are noticed for C–D stretching mode on D atom functionalization. The spectra of sample exposed to only D₂ gas flow with no discharge does not have this band. The peak in the C–H region in this spectra is due to methane impurity in D₂ cylinder that is absorbed by the SWNT during gas flow. The increased C–H peak in the sample exposed to the discharge is due to functionalization of nanotubes by H atom in the D₂ discharge. The source of H atom is the isotopic impurity in D₂. The background spectra of SWNT at the start of the experiment is also shown.

stretching band seen in the 2000 to 2250 cm⁻¹ region is undoubtedly due to functionalization of SWNT by D atoms and the increase in intensity at the C–H region around 2924 cm⁻¹ is also due to functionalization of SWNT by H atoms. The H atom is produced in the discharge from isotopic impurity in D₂. More than double the increase in band intensity of the C–H stretching band for the case with the D₂ discharge compared to the case with only the D₂ gas flow is strong evidence that the H atom available in discharge from the isotopic impurity in D₂ reacts with the carbon of the SWNT. The evolution of C–D peaks at 2100 and 2201 cm⁻¹ demonstrates beyond doubt the functionalization of SWNT by D atoms.

Based on the position of C–D bending mode in chloroform-*d*¹⁷ and other deuterated compounds and on some correlation with the C–H bending in fullerene^{18,19} and amorphous carbon,¹⁶ we expected to find C–D bending vibrations in SWNT in the region 1000–1300 cm⁻¹. Since water bands normally appear in at least part of this wavelength region and the expected C–D bending vibration in our functionalized SWNT with D atom is expected to be very weak, we examined this region on a vacuum Bomem FTIR. Figure 5 is the spectrum of SWNT after exposure to 10 h each of D₂ flow and D₂ discharge. Although the peaks are weak, the existence of these peaks in the expected wavelength region nevertheless indicates the presence of a C–D bending mode.

Direct hydrogenation of SWNT has been studied by quantum chemistry and other theoretical methods²⁰ with the conclusion that the addition of molecular hydrogen to the nanotube is a slightly exothermic process. Atomic hydrogen can chemisorb on CNT sidewalls with a binding energy of ~26 kcal/mol.²¹ The chemisorption and desorption energies of H on CNT, however, depend on the coverage of H on the nanotube. At low coverages, the binding energy of an isolated H might be a little lower than when other H atoms start to

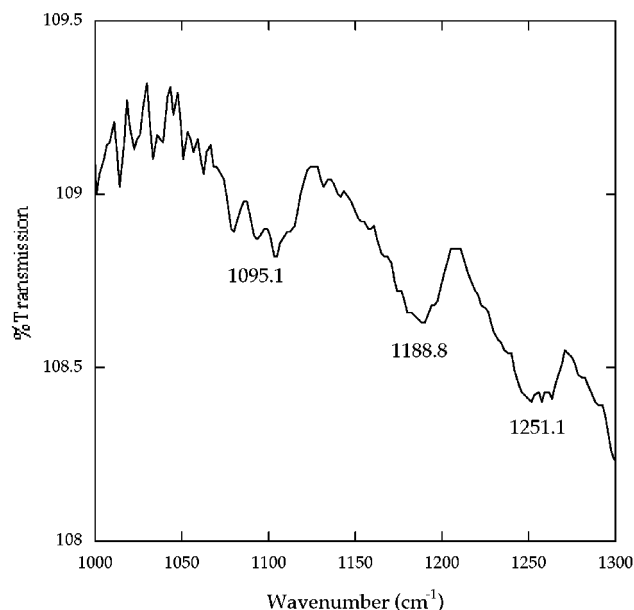


Figure 5. FTIR spectra of SWNTs after exposure to D₂ flow only and to D₂ discharge. The peaks in this region indicate the C–D bending vibrations in SWNT on functionalization by D atoms.

chemisorb on the neighboring sites. At very high coverages, however, H atoms from the neighboring sites could spontaneously desorb as H₂ molecules. We expect, therefore, the system to be in a dynamic equilibrium at an intermediate coverage between the above two limits. The H chemisorption coverage and the FTIR line shapes and positions will not change much after that limiting coverage has been achieved. An indication of the above scenario is that in the experiments we do not observe any change in the spectra when the exposure time is increased from about 30 min to a few hours. More accurate time-resolved data, in future, for exposure times much shorter than 30 min may help to verify the above explanation. On the basis of mechanisms proposed by Kuznetsova et al.,²² it is likely that plasma processing of the SWNT sample creates openings in the sidewalls with dangling –C=C groups that are susceptible to hydrogenation. In this manner the functionalized nanotubes probably have short alkyl groups attached to the sidewalls at these openings. However, there is no clear evidence for such a substitution reaction here.

In conclusion, we have successfully functionalized SWNTs using hydrogen atoms from a microwave discharge. A key parameter was the elimination of the UV component from the discharge. This clean, low-temperature and simple technique has the advantage of giving very clear results compared to wet chemical reactions that can produce polymeric material that produces noise in the transmission spectra. The approach can be used to functionalize nanotubes with other species such as F, NH, etc.

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